RADC-TDR-62-66

SECOND TECHNICAL NOTE

CERAMIC-METAL SEALS FOR HIGH-POWER TUBES

Covering the Period
10 July 1961 through 30 November 1961

ELECTRONIC TUBE DIVISION
SPERRY GYROSCOPE COMPANY
Division of Sperry Rand Corporation
GREAT NECK, NEW YORK

CONTRACT NO. AF30(602)-2371

Prepared for

ROME AIR DEVELOPMENT CENTER
AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE
GRIFFISS AIR FORCE BASE
NEW YORK

10

SPERRY REPORT NO. NA-8250-8268-2

NOVEMBER 1961

RADC-TDR-62-66

SECOND TECHNICAL NOTE

CERAMIC-METAL SEALS FOR HIGH-POWER TUBES

Covering the Period
10 July 1961 through 30 November 1961

ELECTRONIC TUBE DIVISION
SPERRY GYROSCOPE COMPANY
Division of Sperry Rand Corporation
GREAT NECK, NEW YORK

PROJECT NO. 5573
TASK NO. 557303
CONTRACT NO. AF30(602)-2371

Prepared by
ENGINEERING DEPARTMENT
K. H. Styhr

PUBLICATIONS DEPARTMENT
A. S. Ferello

Prepared for

ROME AIR DEVELOPMENT CENTER
AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE
GRIFFISS AIR FORCE BASE
NEW YORK

SPERRY REPORT NO. NA-8250-8268-2
NOVEMBER 1961

COPY NO 07

ABSTRACT

The "ceramic-metal seal for high-power tubes" technology study is a continuation of work initiated under Contract No. AF30(602)-2047, in which 200 metallizing compositions were examined. The variable studies described in the First Quarterly report have undergone a major revision incorporating an analysis of variance of a basic factorial design, in which second, third, and higher order interactions may be evaluated. Ceramic specimens have been received; all tooling, equipment construction, and modifications completed; and the Phase I reliability study started. Experiment No. 1 has been completed and the data are discussed herein. Experiment No. 2 is 50-percent complete.

A non-pumping, cold cathode ionization gage for use as a life test vehicle is described and is being fabricated for testing. Preliminary metallographic data on methods of detection of hermetic leak paths are presented. Decomposition of impregnated carbonaceous materials and metals deposited from a gaseous phase are described as useful methods of leak path determination.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

SECTION I

INTRODUCTION

1-1. PURPOSE OF PROGRAM

This technical note describes the progress of the ceramic-to-metal seal technology study during the second report period of Contract No. AF30(602)-2371. The program is being conducted for the Rome Air Development Center, U.S. Air Force, by the Sperry Gyroscope Company Division of the Sperry Rand Corporation, Great Neck, New York.

The present program is a continuation of the effort initiated under Contract No. AF30(602)-2047, in which 200 metallizing mixtures were examined to determine compositions capable of creating seals as strong as the ceramic member itself. Seals were obtained which have average tensile strengths as high as 21,400 psi. The object of the present effort is to investigate the variables affecting these tensile strengths so that seals with the highest possible reliability can be achieved. In addition, the mechanisms by which vacuum leaks occur are being investigated.

1-2. PHASES OF PROGRAM

The goals of this program are being achieved through seven study phases. Almost all of these phases are intimately dependent upon each other. The work effort during the second report period has been concentrated on Phases I, VI, and VII. These phases are discussed in detail in Section II.

A brief description of the work involved in each of the seven phases is presented in the following paragraphs.

Phase I - Reliability Study - This major phase, which is expected to last for a period of 13 months, is divided into 3 subgroups: (1) sample procurement and equipment alteration, (2) initial variable study, and (3) refined variable study. The majority of this work involves subgroup (2) where an analysis of variance of a basic factorial design is being conducted. This analysis, in which second, third, and higher interactions may be studied, is being used to determine those parameters which have the greatest effect on the reliability of ceramic-to-metal seals.

Phase II - Manual - Using the data generated in Phase I, a detailed guide or manual covering seal technology will be written. Phase I data will be translated into a form most easily assimilated by seal designers and fabricators.

Phase III - Fabrication of Samples - Phase I data, as delineated during Phase II, will be used to fabricate samples for testing during Phases IV, V, and VI.

Phase IV - Environmental Testing - Samples will be tested to determine their resistance to thermal cycling, thermal soak, and high humidity exposure.

Phase V - Tube Compatibility Testing - Samples will be checked to determine the tendency of the seals to produce gases that are harmful to tubes. Electrical testing will be conducted to determine the dielectric loss in the metallized coatings.

Phase VI - Life Testing - This phase will be performed by fabricating, evacuating, and sealing off a ceramic and metal cold-cathode, non-pumping ion gage. Testing will be conducted by reading internal pressures at regular intervals.

Phase VII - Leak Path Study - The objective of this phase is to learn more about the mechanism by which leaks occur. Various penetration and impregnation techniques are being tested through the use of optical, radiographic, and other detection methods.

The technical aspects of these phases were discussed at the Rome Air Development Center on 18 August 1961. Messrs. J. Vanderveer, K. Styhr, and S. Cole represented the Sperry Gyroscope Company and Messrs. D. Bussey and L. Chiosa represented the U.S. Air Force. Additional technical discussions on this program were held at the Sperry Gyroscope Company facility on 25 September 1961 and 27 November 1961. Mr. D. Bussey represented the U.S. Air Force and Mr. K. Styhr the Sperry Gyroscope Company.

SECTION II

DISCUSSION

2-1. PHASE I - RELIABILITY STUDY

a. Procurement and Equipment

(1) Material. A procurement delay from the originally scheduled 15 June 1961 delivery date, until 27 September 1961, when replacement Wesgo ceramics were received, resulted in a delay of over three months in the scheduled start of the reliability study. In addition, both the Wesgo AL 300 and the Coor's AD 995 tensile specimens were slightly out of specification and were, therefore, held by incoming inspection for engineering examination and disposition. Examination revealed that neither the surface area to be metallized nor axial alignment would be affected by these discrepancies. It also revealed that if compensations were made in existing fixturization, the fault would merely place a limitation on the ultimate strength of ceramic-to-metal seals which are measurable by the test method. In order to expedite the program, the parts were accepted and processing started 8 October 1961.

During the delay period, work was almost completely suspended and personnel were directed to other duties. However, equipment modifications and limited trial runs, on modified equipment, continued.

(2) Roller Coater. The following modifications of the roller-coating equipment, from that originally proposed, were found necessary.

- The sample carriage mounting was modified to eliminate sticking
- The metallizing container was modified to eliminate sediment buildup and insure uniform mixing
- The machine body was modified to simplify assembly and expedite cleaning
- The knurling depth on the roller was decreased and an auxiliary roller, acting as an adjustable wiper, was added so that film thickness can be more uniformly controlled.

The modified roller is shown in figure 1. With these modifications, a minimum uniform film thickness of 0.0007 to 0.0008 inch can be applied, which decreases on sintering approximately 20 percent to about 0.0006 inch. The decision was made, therefore, to study metallizing coating thicknesses of 0.0006 inch and 0.0012 inch by a one-coat - two-coat method.

(3) Spray Apparatus. Trial runs were completed on the spray apparatus, consisting of a Paasche-type H air brush. After modifying the masks, to accommodate the out-of-specification tensile specimens received, the spray apparatus, figure 2, was found to function satisfactorily. Little difficulty was experienced in maintaining the coating thicknesses equivalent to those applied by hand painting or roller coating, provided the apparatus is kept in fairly constant use.

(4) Sintering Furnace. The sintering furnace modifications to achieve dew points above room temperature have been completed. Modifications of the temperature control system have been completed and test results indicate that a fixed temperature may be maintained indefinitely or reproduced to ±1°C.

(5) Baldwin Tensile Tester. Modifications and tests to optimize axial alignment, as described in the First Technical Note, have been completed. The first item considered in this study was an examination of the existing test method. Possibilities for misalignment existed in both the Templin grips and the specimen holders. Slippage of the wedges in the Templin grips permitted shifting of the specimen centerline by approximately 0.003 inch. The specimen holders, however, permitted movement up to 0.031 inch.

The Templin grips were replaced by support blocks which were slotted to receive the rods leading to the specimen holders, figure 3. Four rubber pads, whose thickness was slightly greater than the tolerance between the specimen radius and the holder radius, provide positive centering of the specimen. To prevent bending of the top surface of the specimen holder, a radius was added, the thickness was increased, and the bearing area of the support rod was increased.

The new test fixture was tested, using an aluminum reproduction of the test specimen. This reproduction was instrumented with electric resistance strain gages, as shown in figure 3. These gages were mounted in the center of the aluminum specimen (in a vertical direction), at four equally spaced locations around the piece. The purpose of the gages was to indicate if the strain (and thereby the stress) was equal at all points on the specimen. The larger the

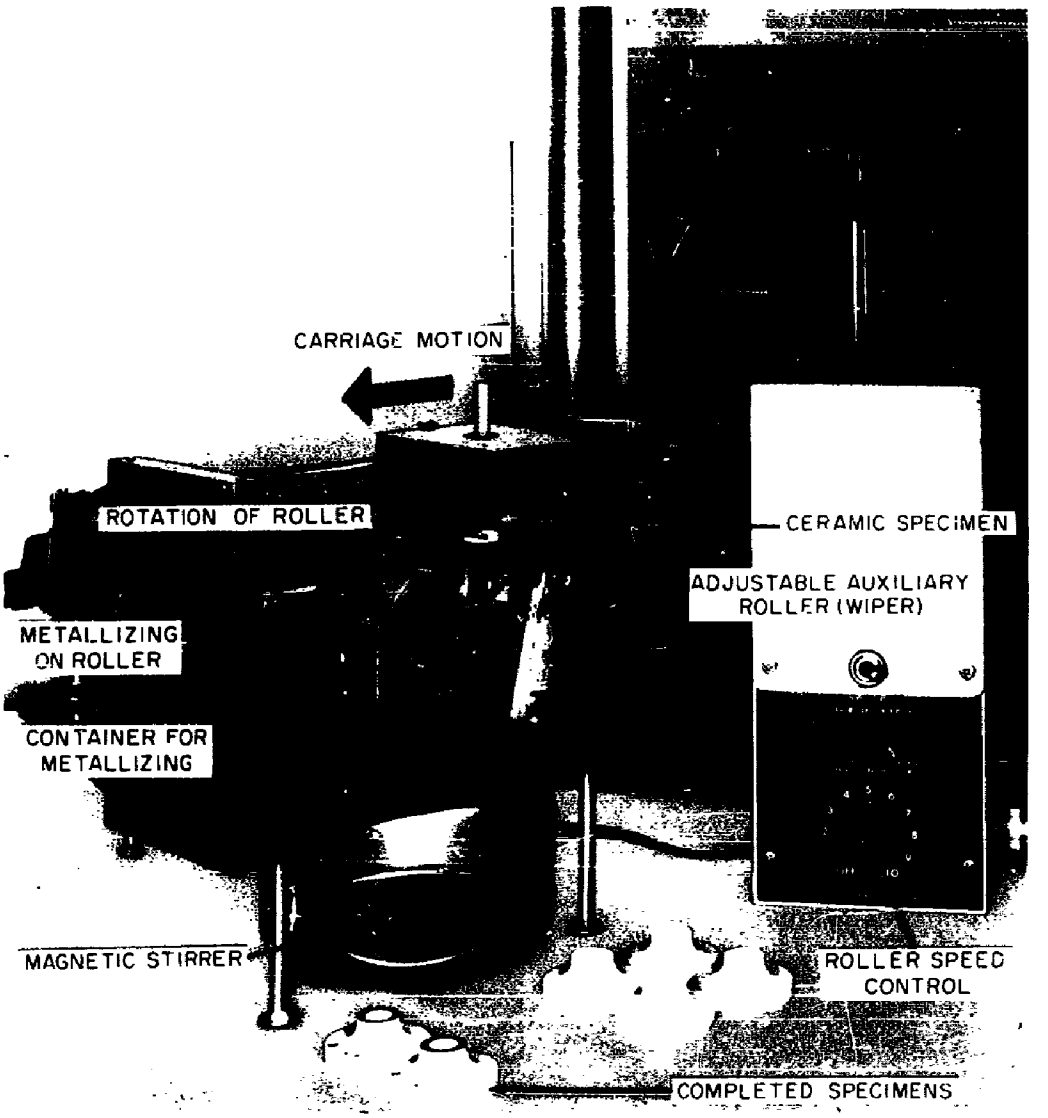


FIGURE 1. ROLLER COATER

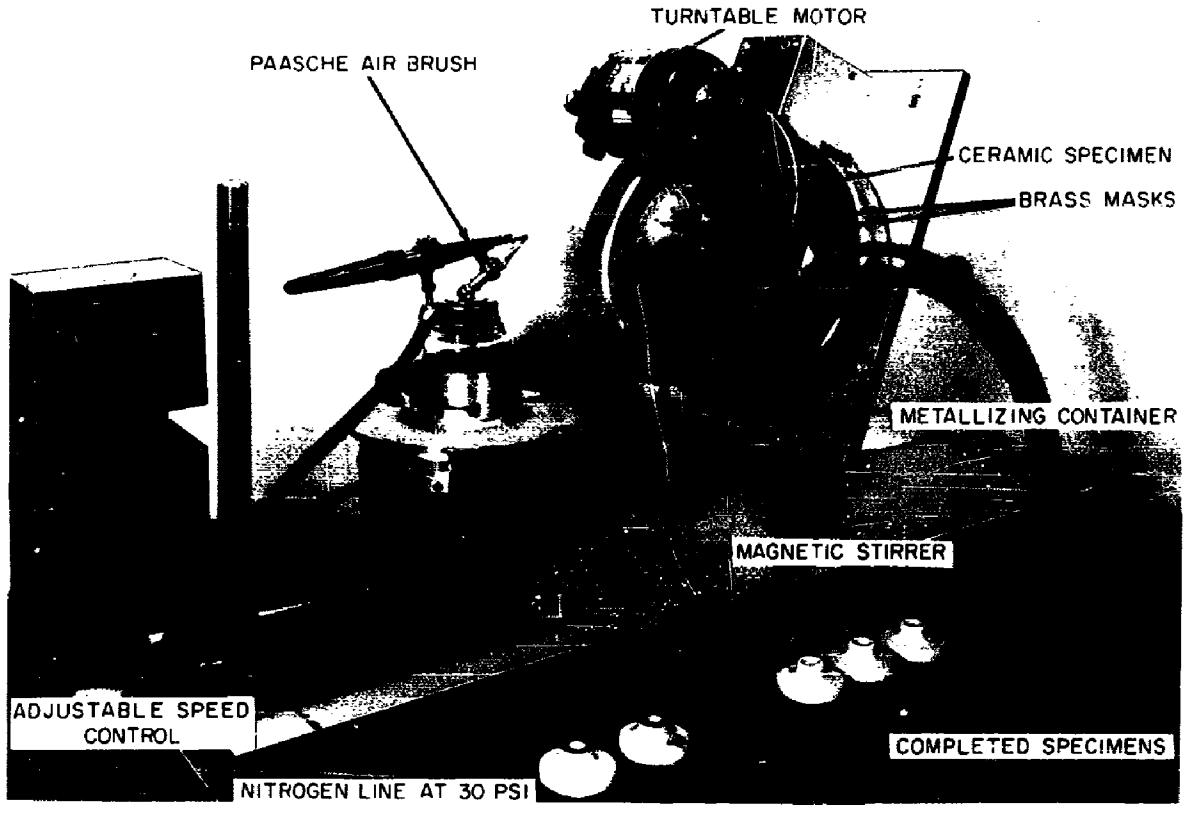


FIGURE 2. SPRAY APPARATUS

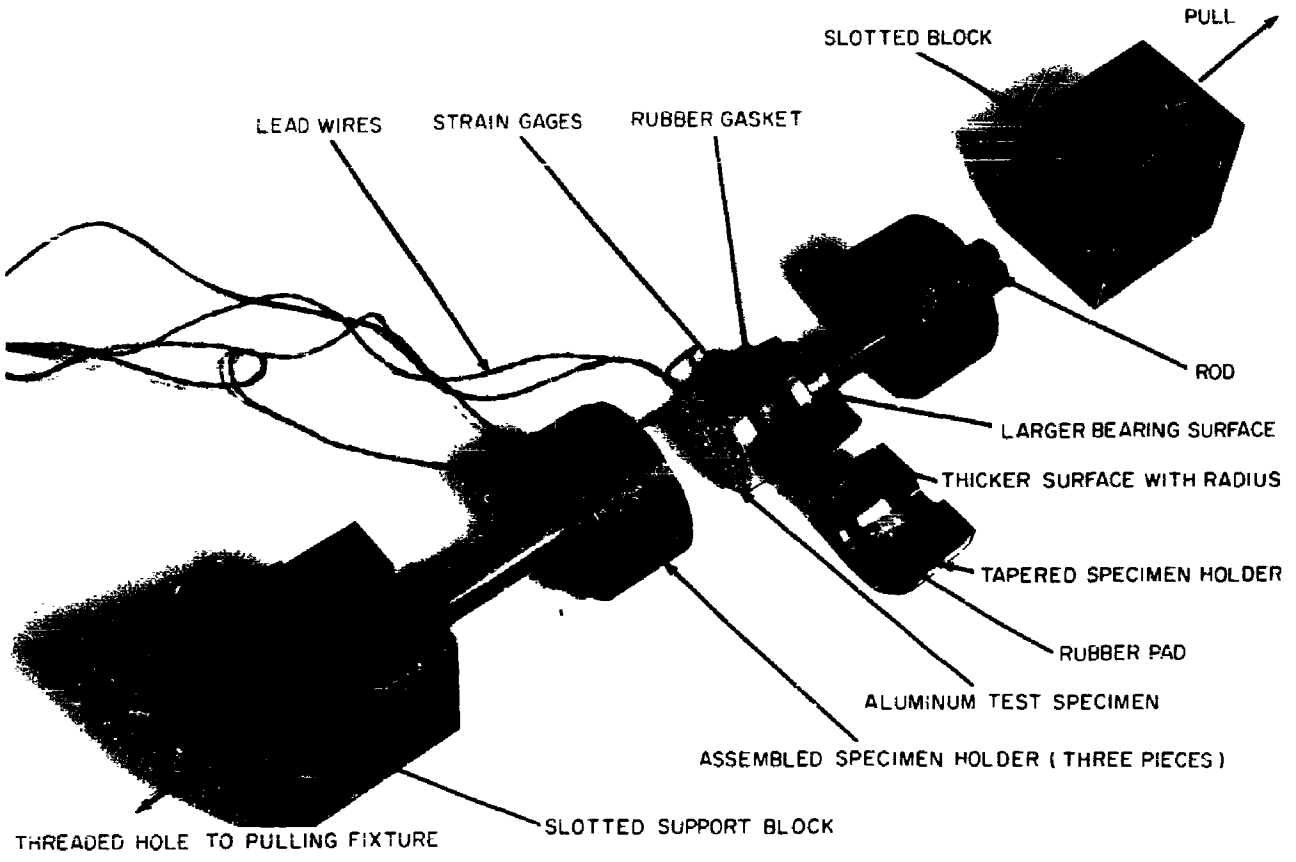


FIGURE 3. MODIFIED SPECIMEN HOLDERS

difference in stress, at various specimen-points, the less meaningful the average stress of the specimen. This condition decreases the accuracy of the results obtained in the tensile tests. Tests were run using both the old and the new support systems.

A comparison of the test results (figures 4A and 4B) shows that the newly designed system represents a substantial improvement over the old system. The first system, using the old grips, yielded an average strain (at 1500-lb load) of 756 micro-inch. The maximum strain, however, was 959 micro-inch, or 26.8 percent above average, while the minimum strain was 341 micro-inch, or 54.9 percent below average. Therefore, the difference in stress, between the maximum and minimum values was

$$\text{Strain} \times \text{Youngs Modulus} = \text{Stress}$$

$$(959 \times 10^{-6} - 341 \times 10^{-6}) \times 10 \times 10^{6} = 6180 \text{ psi}$$

where

$$\text{Youngs Modulus, E, for aluminum} = 10 \times 10^{6}$$

Using the new system (improved grip) an average strain of 761 micro-inch (at 1500-lb load) was noted. The maximum strain was 838 micro-inch, or 10.1 percent above average, and the minimum strain was 714 micro-inch, or 6.2 percent below average. In this case the difference in stress between the maximum and minimum values was

$$(838 \times 10^{-6} - 714 \times 10^{-6}) \times 10 \times 10^{6} = 1240 \text{ psi}$$

In setting up the new grip, it was noted that the legs of the support block had a tendency to bend. The legs were therefore reinforced by 0.25-inch screws (placed through the legs and into the block proper) for the second test. A new support block, as shown in figure 3, with solid walls to prevent bending, has been made and is under test.

b. Initial Variable Study

(1) General Statistical Approach. The improvement of ceramic-to-metal seals may be accomplished by improvement in tensile strength, or by improvement in the reproducibility (reduction of the spread of values around the average strength). Detection of a difference between averages is not difficult if the difference is very large. However, to detect a smaller difference, the spread around the averages must be small. The analysis of variation and covariation, table 1, analyzes the significant differences between averages taking into account the variability around these means. When the difference has been determined for a source of variation, it does not indicate

which condition within the variation is better, but merely that the difference is real and would not occur by chance. The choice of which condition is most suitable must be made by comparing averages.

In order to evaluate the reproducibility of the variable effect, the dispersion of the values around an established average must be measured. When subtracting the lowest value from the highest (table 1, example 2) a range is obtained. This does not necessarily yield a measure around the mean. This disregards the fact that the remaining values were closely grouped about the average or mean. This same range might be obtained from a set of values which have the same mean but are equally distributed through this range (table 1, example 1), or the same range and a different mean (table 1, examples 3 and 4). A standard deviation, however, is a special form of deviation from mean. In this case the difference of each value from the mean is measured, which in turn gives weight to the frequency of occurrence of this difference.

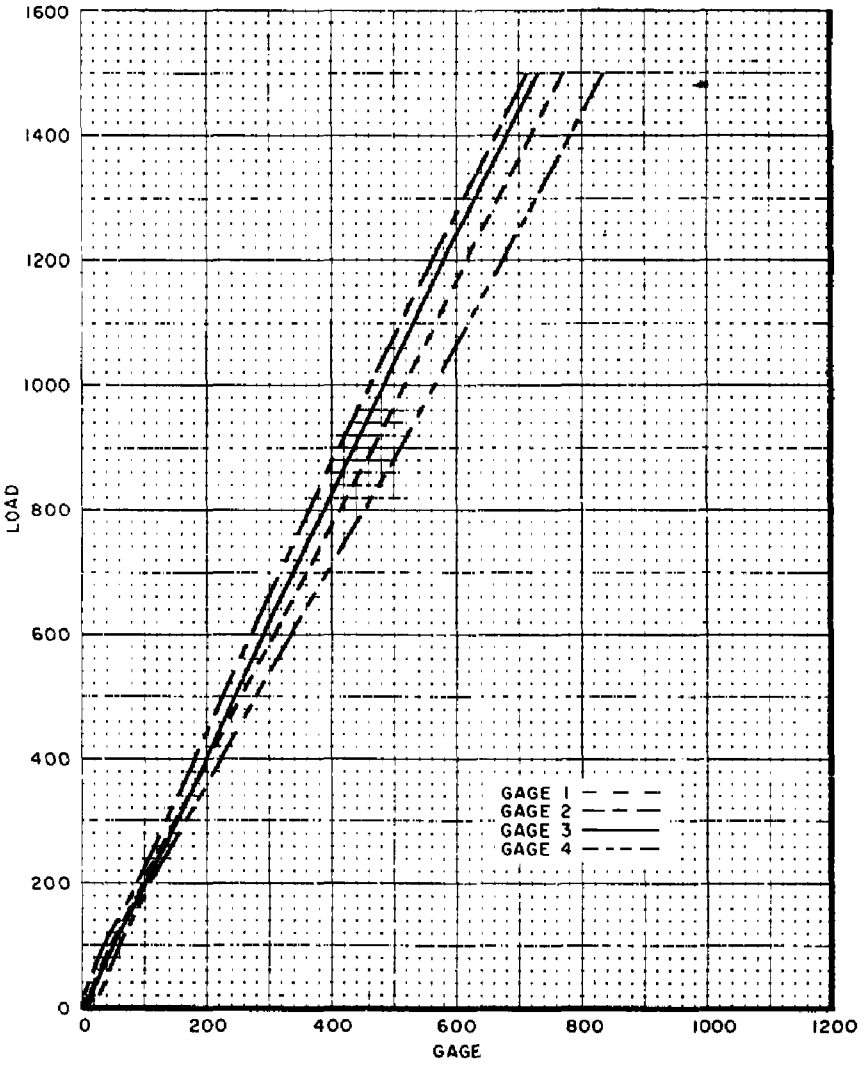
In table 1, examples 1 and 2 have like averages while examples 3, 4, and 5 have a different common average. In all cases, except example 5, the ranges are the same. Comparing standard deviations reveals that examples 1 and 3 are the same while examples 2 and 4 are lower and example 5 is the highest. An evaluation of the reproducibility of these examples results in the following conclusions:

- Examples 2 and 4 were the best (no difference either in range or in standard deviation)
- Examples 1 and 3 were rated next (slightly greater spread)
- Example 5 had the greatest spread.

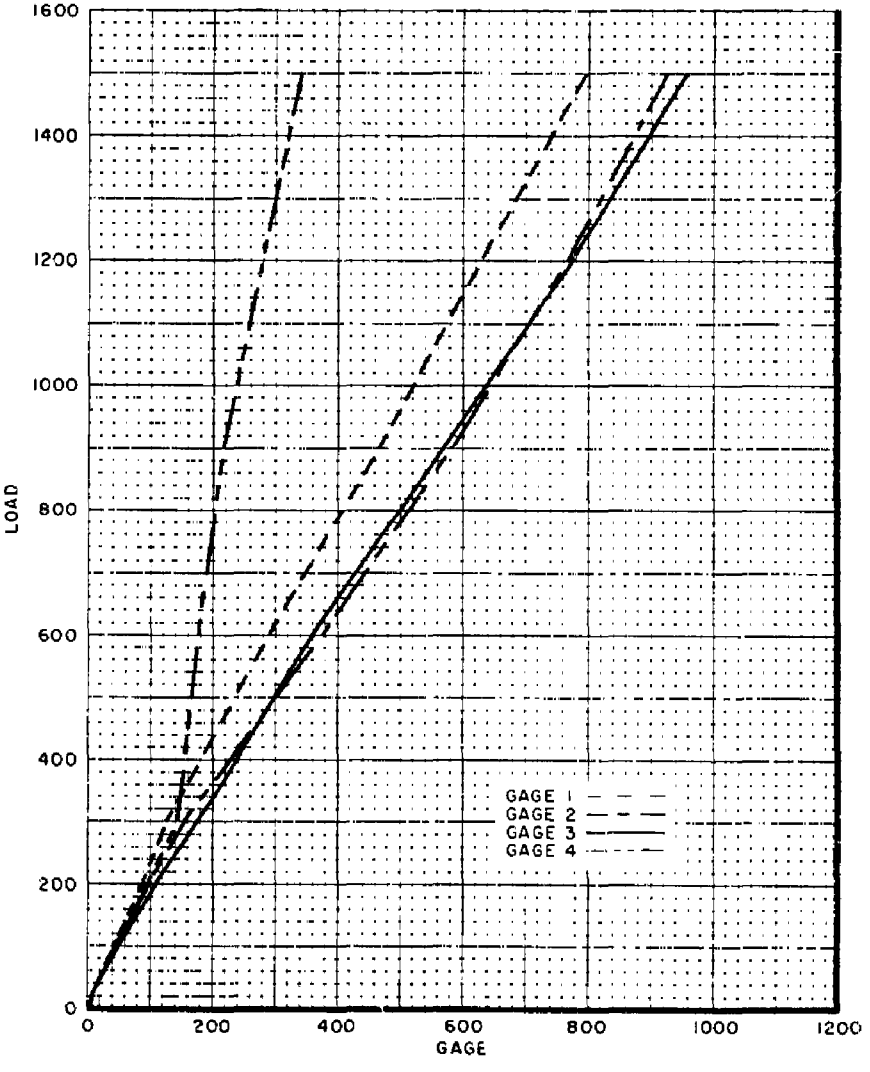
However, in considering reproducibility the spread relative to the average must be considered. The coefficient of variation

$$\frac{\text{Standard Deviation}}{\text{Mean}} \times 100$$

is used in this case. Table 1 reveals the percentile by which each standard deviation varies around its mean. It is significant to note, that none of the examples have the same coefficient of variation. Furthermore, example 5 has a smaller percent-variation around its mean than example 1, which has a lower standard deviation around a lower mean. This is due to the fact that a final reproducibility of ten percent around a small mean will yield a small deviation while the same percentage taken around a large mean will result in a large deviation. Therefore, if the averages are the same the smallest



NEW SUPPORT BLOCKS



OLD TEMPLIN GRIPS

FIGURE 4. CURVES OF OLD AND NEW TEST DATA

TABLE 1

AN ANALYSIS OF VARIATION AND COVARIATION

	Example 1	Example 2	Example 3	Example 4	Example 5
	180	180	1180	1180	700
	250	480	1250	1480	850
	300	485	1300	1485	1000
	350	490	1350	1490	1150
	400	495	1400	1495	1300
	500	500	1500	1500	1500
	600	505	1600	1505	1700
	650	510	1650	1510	1850
	700	515	1700	1515	2000
	750	520	1750	1520	2150
	820	820	1820	1820	2300
Average	500	500	1500	1500	1500
Range	640	640	640	640	1600
Stand. Dev.	218	144	218	144	542
Coef. of Var (%)	44	29	15	10	36

standard deviation may be chosen without further computation. If, however, the averages are far apart, a coefficient of variation comparison, as well as a standard deviation comparison must be made.

An average and a standard deviation together summarize a set of values. The additional advantages of a standard deviation are as follows:

- ±1 standard deviation of the mean will include 68 percent of the measured values
- ±2 standard deviations will include 95 percent of the values
- ±3 standard deviations will include 99.7 percent of the values.

(2) Experiment No. 1. An analysis of the factorial type variance has the following advantages:

- Allows the comparison of more than two simultaneously imposed variables
- Enables the evaluation of interaction effects of these conditions
- Indicates when interactions have statistically significant effects.

Experiment No. 1 was designed as a small initial study in order to accomplish the following:

- Set up experimental procedure
- Test the functioning of experimental equipment
- Familiarize operating personnel with the required degree of precision
- Determine the effects of variables thought to have minimum significance.

It was decided, therefore, to combine experiments Nos. 6 and 7 (first technical note of this contract) and study the effects of two plating baths (P), at two plating thicknesses (T), on two different ceramic bodies (C), as brazed by two different brazing cycles (B). A standard procedure was followed on all specimens and each ceramic was replicated four times.

The detailed design, table 2, indicates that the platings chosen were sulfamate nickel and ammonium nickel, at 0.0002-and 0.0004-inch thicknesses. The first brazing schedule chosen was a

TABLE 2

EXPERIMENT NO. 1-DESIGN DETAIL

Sulfamate Nickel								Ammonium Nickel							
0.0002-inch				0.0004-inch				0.0002-inch				0.0004-inch			
AL 300		AD 94		AL 300		AD 94		AL 300		AD 94		AL 300		AD 94	
1*	2**	1	2	1	2	1	2	1	2	1	2	1	2	1	2
1-1	2	33	34	3	4	35	36	5	6	37	38	7	8	39	40
9	10	41	42	11	12	43	44	13	14	45	46	15	16	47	48
17	18	49	50	19	20	51	52	21	22	53	54	23	24	55	56
25	26	57	58	27	28	59	60	29	30	61	62	31	32	63	64

Metallize: All on one day. Mix 65B. 64 halves AL 300; 64 halves AD 94; 1 coat of metallizing

Sinter: No. 1 First row across all A and B's (32 halves)
No. 2 Second row across all A and B's (32 halves)
No. 3 Third row across all A and B's (32 halves)
No. 4 Fourth row across all A and B's (32 halves)

Plating: Four different conditions sent in four separate times (8 halves at a time) Plating fixtures used: wire.

Brazing: Four separate halves (8 at a time) of each of two brazing conditions

*Brazing schedule No. 1; 10-15-10-10

**Brazing schedule No. 2; 15-15-15-15

10-minute preheat, 15 minutes at brazing temperature, and two 10-minute precool periods. The second schedule was a 15-minute preheat, 15 minutes at brazing temperature, and a two-step cooling of 15 minutes each. AD 94 and AL 300 ceramics were used, and from the design it may be seen that each variation and combination was performed on each ceramic 4 times giving a total of 64 test pieces. The study of this shorter experiment permitted a standard plating, thickness, and brazing schedule to be set up for future tests.

Table 3 shows the raw tensile data in psi. Table 4 lists all the possible combinations of the four main variables and their interactions. For the main variables an average of 32 tensile values found under the heading sulfamate nickel will be compared with 32 tensile values obtained under ammonium nickel. An average of 32 tensile values of 0.0002-inch plating will be compared with 32 tensile values obtained with 0.0004-inch plating. Each main variable (P, T, C, and B) will be compared with 2 averages, each of which is an average of 32 tensile values.

The first-order interaction is the study of the main variables, two at a time, giving a total of six first-order interactions. The initial source of variation (P x T) will compare 4 averages as follows:

- Sulfamate Nickel, 0.0002 inch
- Sulfamate Nickel, 0.0004 inch
- Ammonium Nickel, 0.002 inch
- Ammonium Nickel, 0.004 inch

Each average will include 16 tensile values. Each of the six first-order interactions will be a comparison of 4 averages in each interaction with 16 tensile values making up each average.

In the second-order interaction the variables have been studied three at a time. The interaction P x T x C will compare eight averages as follows:

- Sulfamate Nickel, 0.0002-inch (AL 300)
- Sulfamate Nickel, 0.0002-inch (AD 94)
- Sulfamate Nickel, 0.0004-inch (AL 300)
- Sulfamate Nickel, 0.0004-inch (AD 94)
- Ammonium Nickel 0.0002-inch (AL 300)

TABLE 3

EXPERIMENT NO. 1-RAW DATA (Psi)

Sample No.	Psi	Sample No.	Psi	Sample No.	Psi	Sample No.	Psi	Grand Total $\bar{x}$ = 9001 s = 1998 cv = 22.2%
40	10560	48	7700	56	10780	64	7480	$\bar{x}$ = 9130 s = 1783 cv = 19.5%
39	12870	47	10945	55	9625	63	8910	$\bar{x}$ = 10587 s = 1740 cv = 16.4%
8	9020	16	6765	24	6985	32	4785	$\bar{x}$ = 6889 s = 1731 cv = 25.1%
7	11220	15	10835	23	9625	31	4730	$\bar{x}$ = 9103 s = 2993 cv = 32.9%
38	8965	46	10175	54	10780	62	7700	$\bar{x}$ = 9405 s = 1364 cv = 14.5%
37	11715	45	8360	53	9405	61	6490	$\bar{x}$ = 8993 s = 2179 cv = 24.2%
6	6820	14	8690	22	9020	30	5335	$\bar{x}$ = 7466 s = 1720 cv = 23.0%

TABLE 3

EXPERIMENT NO. 1-RAW DATA (Psi) (Cont)

Sample No.	Psi	Sample No.	Psi	Sample No.	Psi	Sample No.	Psi	Grand Total $\bar{x}$ = 9001 s = 1998 cv = 22.2%
5	9625	13	9020	21	6215	29	8085	$\bar{x}$ = 8236 s = 1489 cv = 18.1%
36	11495	44	6325	52	10725	60	14355	$\bar{x}$ = 10725 s = 3323 cv = 31.0%
35	10890	43	11495	51	7480	59	9790	$\bar{x}$ = 9914 s = 1769 cv = 13.0%
4	8580	12	9185	20	8360	28	7095	$\bar{x}$ = 8305 s = 879 cv = 10.6%
3	10230	11	8360	19	6380	27	8195	$\bar{x}$ = 8291 s = 1573 cv = 19.0%
34	10340	42	8360	50	9845	58	9460	$\bar{x}$ = 9501 s = 842 cv = 8.9%
33	8855	41	10495	49	6655	51	10450	$\bar{x}$ = 9114 s = 1808 cv = 19.9%

TABLE 3

EXPERIMENT NO. 1-RAW DATA (Psi) (Cont)

Sample No.	Psi	Sample No.	Psi	Sample No.	Psi	Sample No.	Psi	Grand Total $\bar{x}$ = 9001 s = 1998 cv = 22.2%
2	13035	10	5500	18	7755	26	10560	$\bar{x}$ = 9213 s = 3283 cv = 35.6%
1	9295	10	9955	18	9900	26	7425	$\bar{x}$ = 9144 s = 1184 cv = 13.0%
	$\bar{x}$ = 10220 s = 1648 cv = 16.1%		$\bar{x}$ = 8885 s = 1735 cv = 19.5%		$\bar{x}$ = 8721 s = 1612 cv = 18.5%		$\bar{x}$ = 8178 s = 2457 cv = 30.1%	

TABLE 4

EXPERIMENT NO. 1-ANALYSIS OF VARIANCE

No. of averages	No. of tensile values in each average	Source of Variation	Sums of Squares	Degrees of Freedom	Mean Square (Variance)	F ratio
2	32	Plating baths (P)	4,834,500	(P-1) = 1	4,834,500	1.33
2	32	Thickness of plating (T)	876,560	(T-1) = 1	876,560	
2	32	Ceramics (C)	28,743,000	(C-1) = 1	28,743,000	7.88**
2	32	Brazing schedules (B)	1,887,190	(B-1) = 1	1,887,190	
4	16	P x T	452,268	(P-1) (T-1) = 1	452,268	
4	16	P x C	1,123,609	(P-1) (C-1) = 1	1,123,609	
4	16	P x B	7,049,031	(P-1) (B-1) = 1	7,049,031	1.90
4	16	T x C	5,796,068	(T-1) (C-1) = 1	5,796,068	1.56
4	16	T x B	2,168,265	(T-1) (B-1) = 1	2,168,265	
4	16	C x B	2,333,263	(C-1) (B-1) = 1	2,333,263	
8	8	P x T x C	1,894,045	(P-1) (T-1) (C-1) = 1	1,894,045	

TABLE 4

EXPERIMENT NO. 1-ANALYSIS OF VARIANCE (Cont)

No. of averages	No. of tensile values in each average	Source of Variation	Sums of Squares	Degrees of Freedom	Mean Square (Variance)	F ratio
8	8	P x T x B	3,390,186	(P-1) (T-1) (B-1) = 1	3,390,186	
8	8	P x C x B	169,107	(P-1) (C-1) (B-1) = 1	169,107	
8	8	T x C x B	664	(T-1) (C-1) (B-1) = 1	664	
16	4	P x T X C x B	204,794	(P-1) (T-1) (C-1) (B-1) = 1	204,794	
4	16	Replicates (R) (Error)	190,571,500	(P x T x C x B) (R-1) = 48	3,970,239	
1	64	Total	251,494,050	(P x T x C x B x R-1) = 63		

- Ammonium Nickel 0.0002-inch (AD 94)
- Ammonium Nickel 0.0004-inch (AL 300)
- Ammonium Nickel 0.0004-inch (AD 94).

Each average will include 8 tensile values taken from 2 columns with 4 values in a column. Each second-order interaction will compare 8 averages of 8 values each.

The third-order interaction of all 4 main sources of variation yields 16 averages represented by the 16 columns of table 2, with 4 tensile values in each column. The replication variable will have 4 averages represented by each row of table 2 with 16 tensile values in each row. The number of averages computed comes to a total of 85 based on merely the 64 tensile values used for the entire experiment.

In evaluating data from the mean squares, table 4, replicate variance includes any residual variation in technique and is termed error. The amount of information gained from the experiment is determined by the error. When the error variance, table 4, is high few sources of variation will prove statistically significant unless the source of the measured variation is extremely large.

The size of the error variance determines how small a variation may be detected. Starting with the third-order interaction (P x T x C x B), the variance of the source of variation is divided by the error variance to obtain an F ratio. The F ratio tables are consulted using the degrees of freedom for the source variance and the degrees of freedom for the error term. All variance values less than the error term will not be significant. With the 1 degree of freedom for the source of variation and 48 degrees of freedom for the error, a value of at least 4 must be obtained for the F ratio to have significance.

Only the variation in ceramics proved to be significant. The level of risk, taken in stating that the two ceramics are different, is less than 1 chance in 100, or 1 percent. The F ratios are marked in table 4 with asterisks to indicate the level of significance: 5 percent*; 1 percent** and 0.1 percent***. To have a 0.1-percent level of risk for the ceramic, the F ratio has to be greater than 12. If the F ratio is 4.04, a risk of accepting a real difference, when none exists, occurs 1 out of 20 times. The greater the level of significance, the less risk is run in accepting the fact that the source of variation causes real differences. The average of 32 samples for AD 94 is 9671 and the average of 32 AL 300 samples is 8331. The average tensile values of

AD 94 are better than those of AL 300. Since tests on both ceramics will continue in the future there will be further opportunity to verify the results.

An interesting fact brought out by the design is the systematic drop in averages of the four replicates (10, 220, 8885, 8721, 8178). This may account for the large variance in replication. This indicates the possibility of a deterioration of tensile value as a function of time. The time element may be between metallizing and sintering, sintering and plating, or plating and brazing. Apparently it is not related to metallizing, since the samples were metallized in numerical order, and the process was completed in one day. No decrease in tensile values, relating to increasing sample numbers was noted. The second experiment is in progress, and if this indication is repeated, the time element will be studied as a separate experiment, prior to the third planned experiment. Further decrease of the experimental error is expected with the use of a clip rack for plating, rather than the method of wiring used in the first experiment.

It should be noted that the following data are always recorded:

- Date on which each specimen was metallized, sintered, plated and brazed
- Which specimens were metallized, sintered, plated, and brazed at the same time.

Although this analysis of variance showed no other significant source of variation, one complete set of conditions must be chosen for future experiments.

Sulfamate nickel plated to a 0.0002-inch thickness and the first brazing schedule has been chosen as the procedure for both types of ceramics. In table 2 this is represented by column 1 for AL 300, and column 3 for AD 94. Their averages are similar, and are close to the grand average of 9001 psi. If the columns that gave the best reproducibility had been chosen, sulfamate nickel at a thickness of 0.0002 inch and with braze schedule No. 2, would be used for AD 94; while sulfamate nickel at a thickness of 0.0004-inch with braze schedule No. 2, would be used for AL 300. It is considered necessary in this case, to use the same conditions on both ceramics in order that all ceramics undergo the same treatment (except for the imposed variations in future experiments). However, several samples will be retested, at the conditions which gave the least variation for each ceramic, to determine if the spread is consistently lower. Another basis for choice is that sulfamate nickel requires a shorter plating time than ammonium nickel. Furthermore, the 0.0002-inch plating takes half the time

required by the 0.0004-inch plating, and the first brazing cycle is 15 minutes shorter. This will enable a shortening of the time element, which might be affecting replication.

(3) Experiment No. 2. Experiment No. 2 (table 1, First Technical Note under this contract) is already in progress. The outline design consists of the following:

No. of Items	Source of Variation	Abbreviations
2	Ceramics	C
3	Applications	A
3	Ball milling times	B
2	Coatings (layers)	L
6	Replicates	R

The two ceramics are AL 300 and AD 94. The methods of application to be studied are roller coating, spraying, and hand painting. A single metallizing mix 65B, the same formula as was used in Experiment No. 1, will have been ball milled for two days, five days, and ten days to study the effect of the particle size on the metallizing. The number of coatings to be applied are one layer or two layers.* All conditions are to be replicated six times. Table 5 lists the design detail for the total number of 216 tensile tests (2 x 3 x 3 x 2 x 6).

The specimen coding system used in Experiment No. 1 will be followed for all future experiments. For example: the coding symbol 2-39-B (experiment 2-sample 39-specimen half B) allows determination of which half of the tensile specimen was on the bottom during brazing process. Since all brazing is done with the B half at the bottom, a systematic fracture pattern, if one if found to exist, can be related to brazing orientation. The foregoing example (2-39-B), for instance, reveals the following (table 5)

- AL 300 ceramic
- Replicate 4
- 2 coats of mix-65B
- 5 days milling
- Application by roller coater.

*The third coating or layer condition was deleted because of equipment limitations with a resulting reduction of 108 tensile tests for this equipment.

TABLE 5

EXPERIMENT NO. 2-DESIGN DETAIL

AL 300																	
Roller						Spray						Paint					
65B-2*		65B-5		65B-10		65B-2		65B-5		65B-10		65B-2		65B-5		65B-10	
1**	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2
1	13	25	37	49	61	73	85	97	109	121	133	145	157	169	181	193	205
2	14	26	38	50	62	74	86	98	110	122	134	146	158	170	182	194	206
3	15	27	39	51	63	75	87	99	111	123	135	147	159	171	183	195	207
4	16	28	40	52	64	76	88	100	112	124	136	148	160	172	184	196	208
5	17	29	41	53	65	77	89	101	113	125	137	149	161	173	185	197	209
6	18	30	42	54	66	78	90	102	114	126	138	150	162	174	186	198	210

AD 94																	
Roller						Spray						Paint					
65B-2*		65B-5		65B-10		65B-2		65B-5		65B-10		65B-2		65B-5		65B-10	
1**	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2
7	19	31	43	55	67	79	91	103	115	127	139	151	163	175	187	199	211
8	20	32	44	56	68	80	92	104	116	128	140	152	164	176	188	200	212
9	21	33	45	57	69	81	93	105	117	129	141	153	165	177	189	201	213
10	22	34	46	58	70	82	94	106	118	130	142	154	166	178	190	202	214
11	23	35	47	59	71	83	95	107	119	131	143	155	167	179	191	203	215
12	24	36	48	60	72	84	96	108	120	132	144	156	168	180	192	204	216

*This row across indicates ceramic application mix no.

**This row across indicates the number of coats applied.

(4) Experiment No. 3. Experiment No. 3 incorporated the experimental designs listed in the First Technical Note under this contract (tables 2 and 4). Since the furnace being used has an automatic feed, variation in the heating rate varies the soak time. It was more desirable to study heating rate interaction with sintering temperatures. There are 15 ceramic and mix combinations. However, neither ceramics nor mixes can be evaluated by themselves. Various mix compositions as well as a various number of mixes will be tried on different ceramics. This will be listed as source of variation, ceramic and mix with 15 items. The outline form of experiment No. 3 is as follows:

No. of Items	Source of Variation	Abbreviations
3	Sintering temperatures	S
15	Ceramic and mix	X
3	Heating rates	H
4	Replicates	R

This experiment will require 540 (3 x 15 x 3 x 4) tensile tests, as shown in table 6. It is expected that the reduction in the replication will be outweighed by the advantage gained in studying 15 ceramic and mix combinations at a sintering temperature of 1425, 1500, and 1575°C, and at a heating rate cycle of 4, 6, and 8 hours. The design details of further experiments have not been finalized to date, but will be reserved until the results of the first two or three experiments have been analyzed.

2-2. PHASE VI - LIFE TESTING

A life test is necessary for a proper quality evaluation of a hermetic seal between ceramic and metal surfaces. One such test allows a differential gas pressure (between two chambers so separated) to be measured at regular intervals over a long period of time. Helium penetration, at a normal differential pressure of 1×10^{-5} mm of Hg, as detected over a short period of time by use of a mass spectrometer is not sensitive to very small leaks. Normal ionization gages contain filaments which, when initially heated, emit large quantities of gas (relative to gas already in evacuated chambers).

TABLE 6

EXPERIMENT NO. 3-DESIGN DETAIL

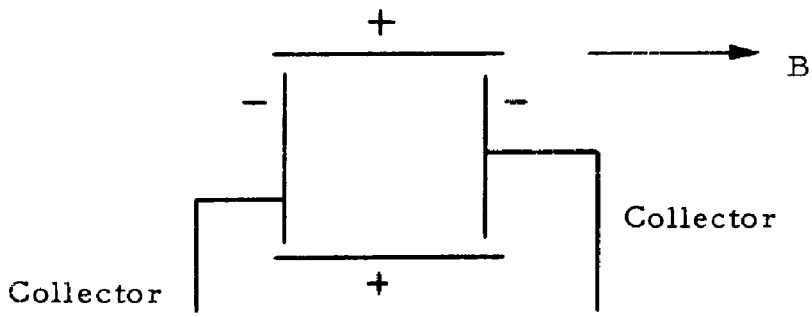
1425°C			1500°C			1575°C		
4 hr*	6 hr*	8 hr*	4 hr	6 hr	8 hr	4 hr	6 hr	8 hr
1**	2	3	4	5	6	7	8	9
10	11	12	13	14	15	16	17	18
19	20	21	22	23	24	25	26	27
28	29	30	31	32	33	34	35	36

*4 hr, 6 hr, and 8 hr represent heating rates.

**Each numbered box represents 15 combinations of ceramics and mixes. Each row across represents a replicate (one sample at every condition).

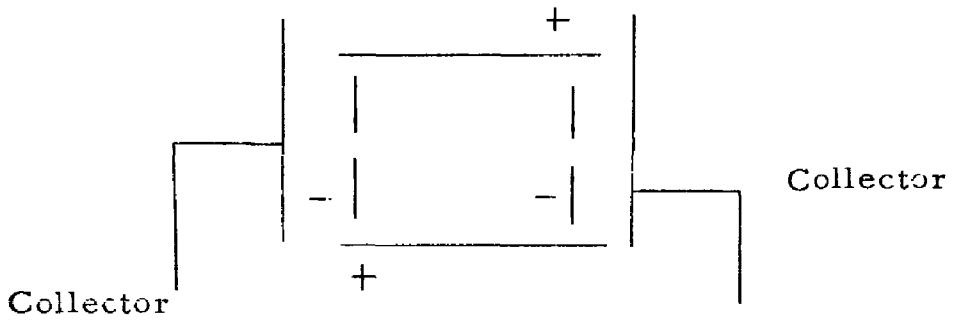
Such gages, however, have a pumping action which, in a finite length of time, restores the chamber to a pressure level equal to and eventually better than that which originally existed. Cold cathode gages have been designed in order to eliminate the first problem. However, the need for a non-pumping ionization gage has given rise to a proposed redesign of a Penning gage, specifically to meet the objectives of this program.

A Penning cell consists of electrodes in the following configuration



Electrons emitted from the cold cathode, or found in the volume, are deflected by means of a magnetic field to move in a tight circle perpendicular to that magnetic field. The electric field configuration causes the electrons to move with a periodic type motion between the cathodes. The resulting motion is a tight helix whose axis is parallel to the direction of the magnetic field. As the electrons spiral, they collide with neutral gas atoms forming positive ions and electrons. The ions will travel directly to the cathode to be collected. The newly formed electrons continue to spiral. Space charge limitation controls the number of electrons which spiral. Scattering by collisions allows the electrons which are in excess of the limit to be collected by the anode. The magnitude of the total current, which is the sum of the positive ion current to the cathode and the electron current from the same electrode, is used as a measure of the gas pressure present.

Pumping in a Penning cell will occur when gas ions react with the cathode to form stable compounds or when gas ions are driven into the collecting electrode with moderately high energy. The essential feature of the non-pumping gage is the collector as shown on the following page.



Instead of using the cathode as a collector, a special central hole cathode is used with a separate collector. Most ions pass through the hole because of the field configuration. A retarding voltage between the cathode and the collector reduces the kinetic energy of the ions so that ions will not be pumped by being driven into the cathode. The collector is gold-plated to eliminate chemical reactions on the surface. Therefore, little pumping will occur on the collector surface because of chemical reactions or surface bombardment.

A gage of the approximate dimensions shown in figure 5 is being fabricated and tested as part of the contract. If proven successful, this gage will be used as the life test vehicle required for this phase of the program.

2-3. PHASE VII - LEAK PATH STUDY

a. Approaches and Calculations

An understanding of the mechanism by which leak paths occur is essential to the production of reliable seals. It is apparent that the mere detection of a leak will not help in this understanding, and it therefore becomes necessary to provide a method by which the leak path may be observed. In an effort to obtain a suitable method, the previous work on dye penetration and fluorescent oil penetration has been expanded. The list below includes all suggested methods, most of which have been investigated. Some of the suggested methods have been eliminated for various reasons which are discussed in Paragraphs b and c.

METHODS CONSIDERED FOR LEAK PATH TRACING

A. Substances Detectable by Sectioning

I. Liquids
   a. Dye penetrant (Metal Check)
   b. Fluorescent oil (Zyglo)

METHODS CONSIDERED FOR LEAK PATH TRACING (Cont)

II. Solids resulting from liquid penetration or decomposition
  a. Carbon decomposition product
    - Sucrose solutions (sugar)
    - Dye penetrant
    - Animal and vegetable micro-organisms
  b. Metals and/or alloys
    - Molten indium
    - Mercury

III. Solids resulting from gaseous decomposition
  a. Metals (Ni from nickel carbonyl)
  b. Carbon (pyrolysis of methane)

B. Substances Detectable by Other than Visual Means

I. Radiographic detection of high-density materials (lead acetate)

II. Autoradiographic detection methods

C. Ultrasonic Flaw Detection

Before any further testing was initiated, the leak rate of 38 test pieces was determined. This was done by measuring the pressure increase in microns during a 30-second time interval. An approximation of the leak diameters was then made using Poiseulle's Equation for viscous flow. This is applicable when the leak diameter is larger than the mean free path of air. The equation which resulted after making certain assumptions and approximations was

$$D = 3.49 \times 10^{-5} \Delta P$$

where D is the leak diameter in cm and ΔP is the observed pressure increase in microns.

This calculation was done to provide an order of magnitude value for the leak diameters, since very small leaks would prohibit the use of certain proposed methods. The calculation showed diameters of 6×10^{-5} cm for a measure ΔP of 10 microns.

These calculations were pursued even though the leak paths vary in length and probably contain a series of leaks rather than one single leak. The results indicate only a relative value for the test vehicle, not an absolute value for a single leak.

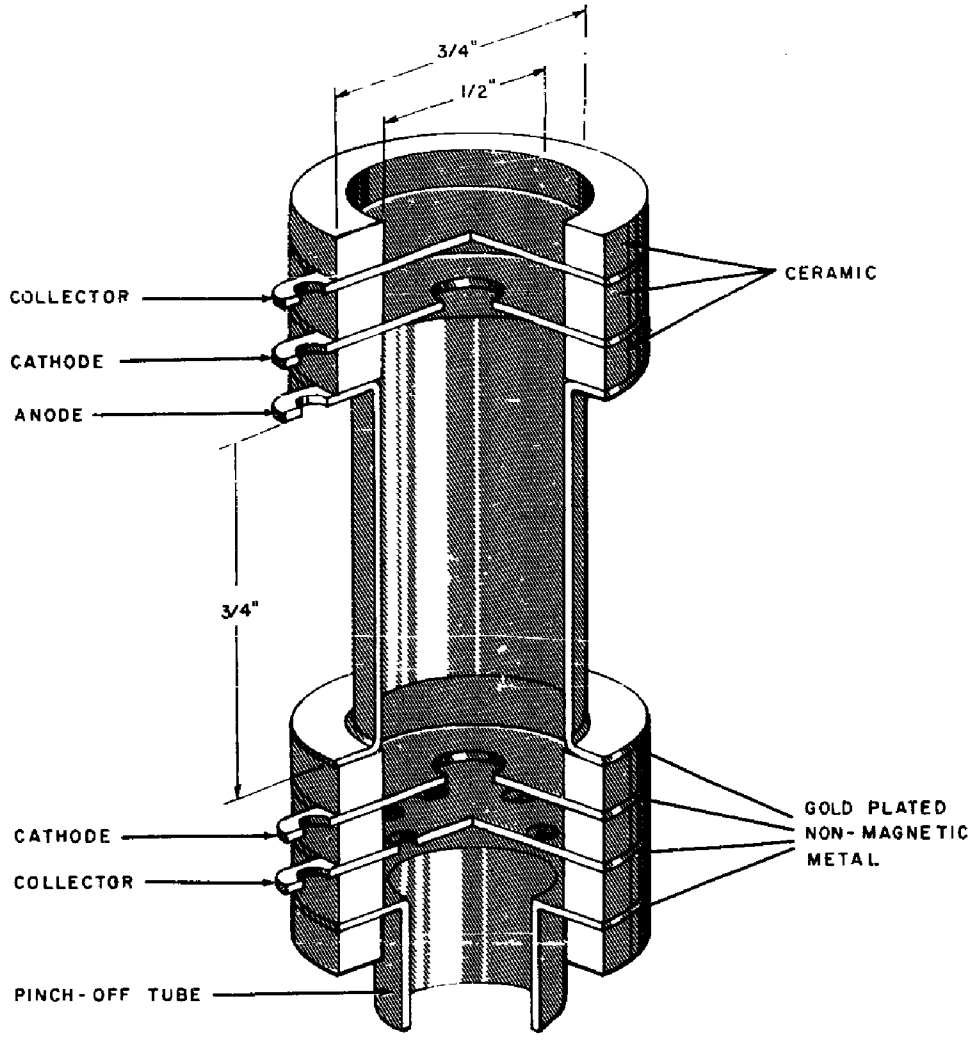


FIGURE 5. NON-PUMPING COLD CATHODE ION GAGE

b. Results of Metallographic Examination

(1) Decomposed Dye Penetrant Several specimens exhibiting leaks were filled from one end with dye penetrant. Time was allowed for the dye to penetrate through the leak and appear on the opposite end. Those samples which showed penetration of the dye were baked in air at 275°F for 1/2-hour in order to decompose the vehicle. This temperature was decided upon after trial bake-outs at 500, 400 and 300°C. Samples treated in this manner were potted for metallographic sectioning. The technique for finding the leak path was to polish down toward the face of the ceramic, from the penetrant exit side. An accumulation of decomposed dye penetrant (carbonaceous material) usually indicated the leak path location, figures 6 and 7. It should be noted that in figures 6 and 7 the voids indicated are obviously filled with a residue. Once the location of the leak path was determined, the sample was repotted and sectioned in the longitudinal direction in an attempt to see the entire length of the leak path. A longitudinal section through the voids shown in figure 6 is depicted in figure 8. In many cases, because of the brittle nature of the deposit, the carbonaceous material was lost during polishing. It was found that the location and shape of the carbonaceous residue could be determined by etching the metal (particularly if the voids occurred in the braze material) leaving the residue in relief, figure 9.

(2) Sucrose Solution. This method is similar to the first. It depends upon the decomposition of a liquid trapped in a leak path. The resulting solid which remains in the leak path can usually be located during sectioning. Due to the higher surface tension and viscosity of the sugar solution it was necessary to force the liquid into the leak by direct application of pressure. The obvious drawback of this liquid, when compared to the dye penetrant, is the procedure required to introduce the liquid, and the restricted size of the leak which can be penetrated. This method was tried on several samples exhibiting gross leaks. Decomposition of the sugar solution was attained by air drying, heating to 100°C for 1 hour, raising the temperature to 350°C, and then cooling. This was followed by hydrogen firing at 900°C for 5 minutes. Three samples were then sectioned as previously described. A carbonaceous material was observed in the leak path. However, because of the large size of the leak path and the brittle nature of the deposit it was difficult to obtain a polished sample suitable for photomicrography.

(3) Metal Acetylacetonate ($M^{x}(C_5H_7O_2)_x$). This method shows promise in that the penetrating material is a gas and the residue produced is a metal. Metals give a much higher contrast than the

carbonaceous materials when viewed metallographically and are more easily identifiable. Furthermore, no special techniques are required during polishing as is the case with the brittle carbonaceous materials. In a trial run, nickel was deposited on the wall of a glass test tube with a total build up of approximately 60 x 10^{-6} inch. This indicates that it is entirely possible to introduce this metal into most leaks. Figure 10 illustrates the type of deposit obtained. This metal film was taken from the glass tube mentioned.

An apparatus has been constructed, figure 11, in which the sublimation of this material will take place in a closed container, the only leak paths being those through the specimens. Attempts will be made using a pressure differential to pull the gas through the leak where it will be decomposed.

Tests are currently being conducted to determine the temperatures required for both sublimation and decomposition of the nickel and copper salts. It might be mentioned that the metal acetylacetonates were chosen instead of the well known metal carbonyls because of their less toxic properties.

c. Other Approaches

(1) Dye (MET-L Check) and Fluorescent Oil (Zyglo) Penetrants. A total of 6 samples were treated with Zyglo and over 20 with MET-L Check. These two series of tests produced similar results. Most leaks are penetrated and these materials can be observed on the face of the ceramic at low magnification. The exact location of the leak is, however, difficult if not impossible to observe since the entire ceramic face becomes coated. This is due to the low surface tension of the materials in question.

Even when the leak can be located and a section is made, problems still exist, since the polishing operation requires the use of vehicles, the penetrants can be washed or abraded away. If the penetrant is not removed it still possesses the ability to creep and may fill voids or cracks inadvertently created during polishing. If all of the afore mentioned problems could be overcome, there would still be one difficulty which would preclude the use of these penetrants. High power magnification must eventually be employed to observe the leak path. Since these penetrants are not observable above 40X magnification due to the type of illumination employed, they are of little use.

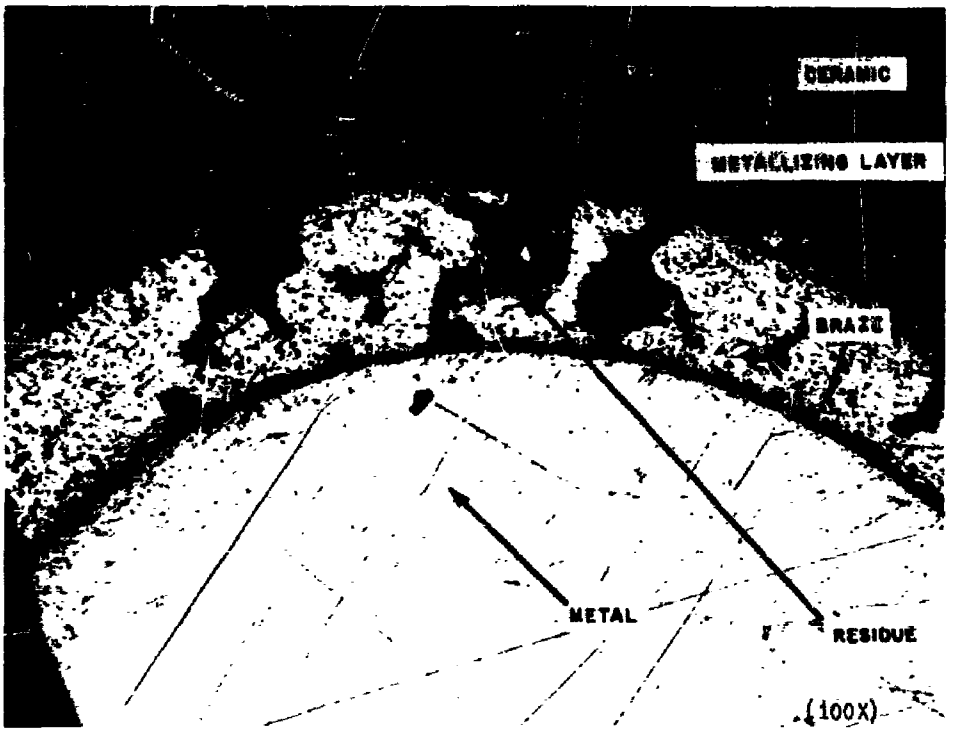


FIGURE 6. PHOTOMICROGRAPH OF LEAK PATH CROSS SECTION, SHOWING PRESENCE OF RESIDUE

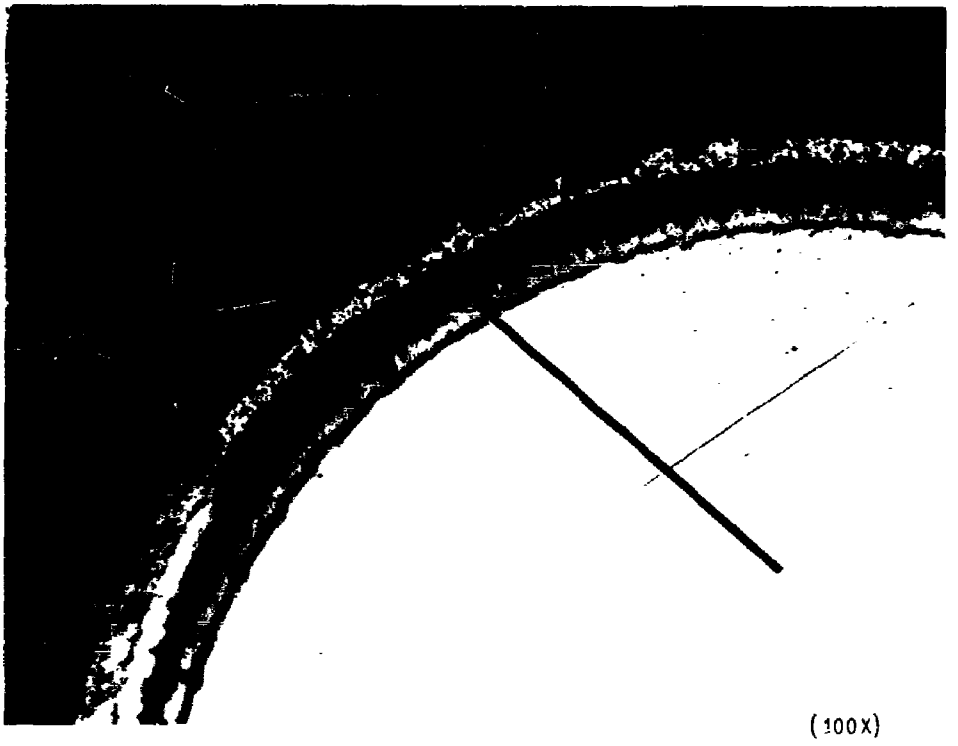


FIGURE 7. PHOTOMICROGRAPH OF LEAK PATH CROSS SECTION, SHOWING POROUS BRAZE

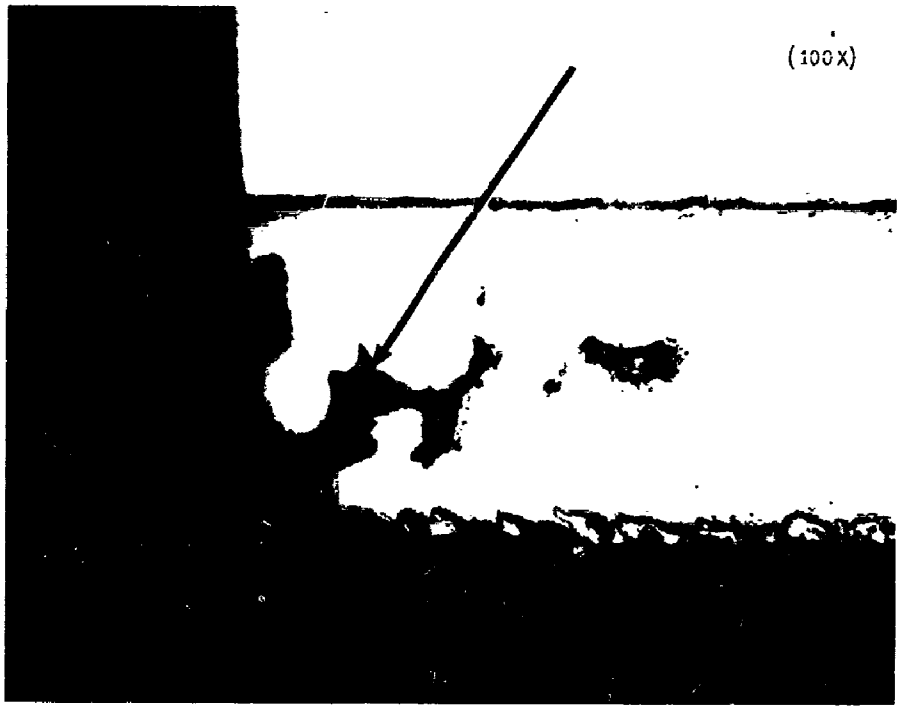


FIGURE 8. PHOTOMICROGRAPH OF LONGITUDINAL SECTION THROUGH POROUS BRAZE

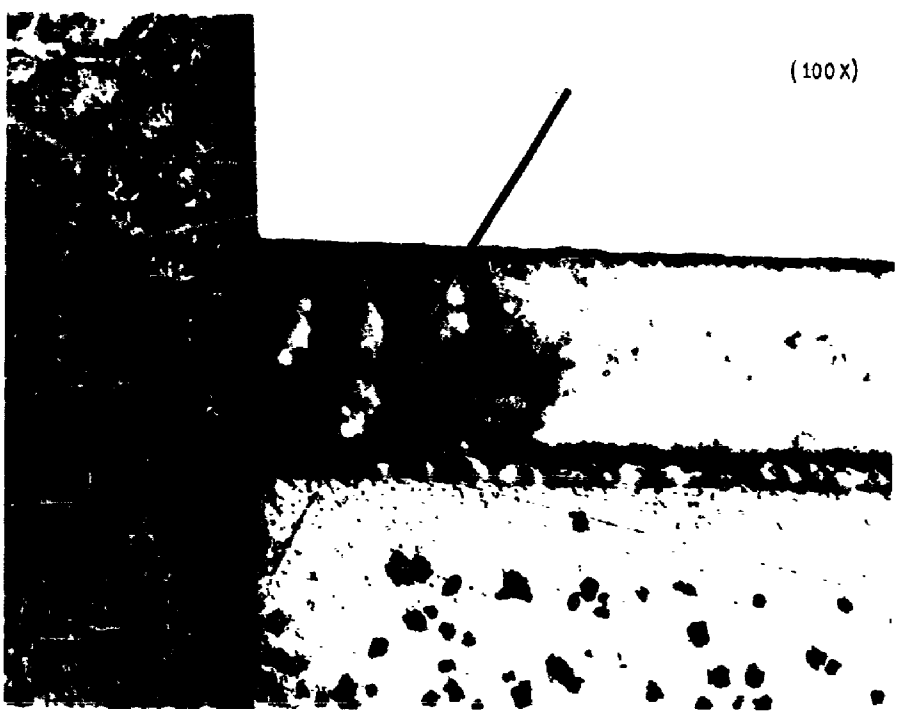
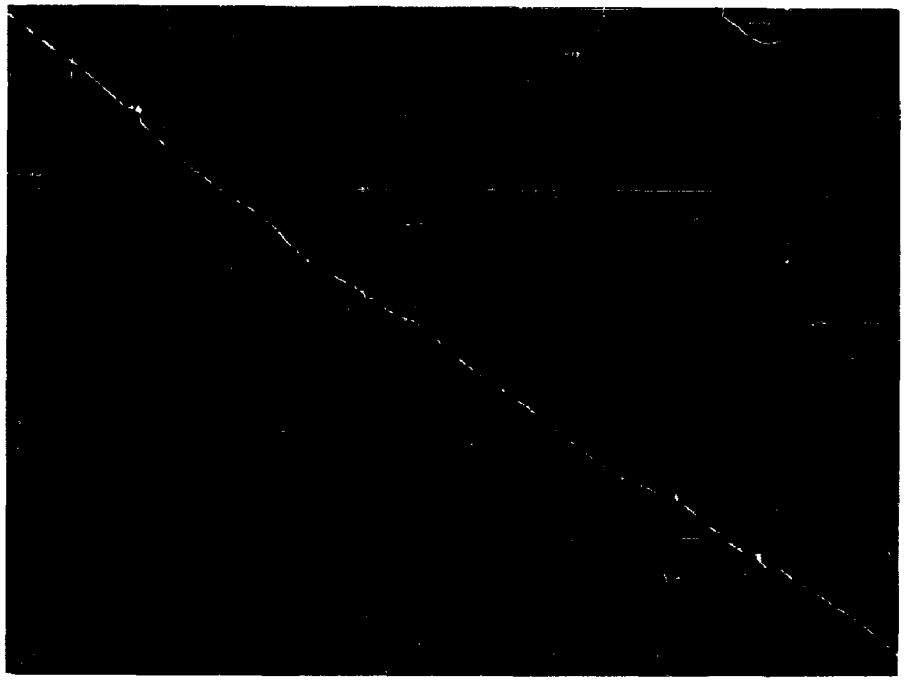


FIGURE 9. PHOTOMICROGRAPH SHOWING CARBONACEOUS RESIDUE AFTER ETCHING



(200X)

FIGURE 10. PHOTOMICROGRAPH OF NICKEL DEPOSITED FROM A GAS

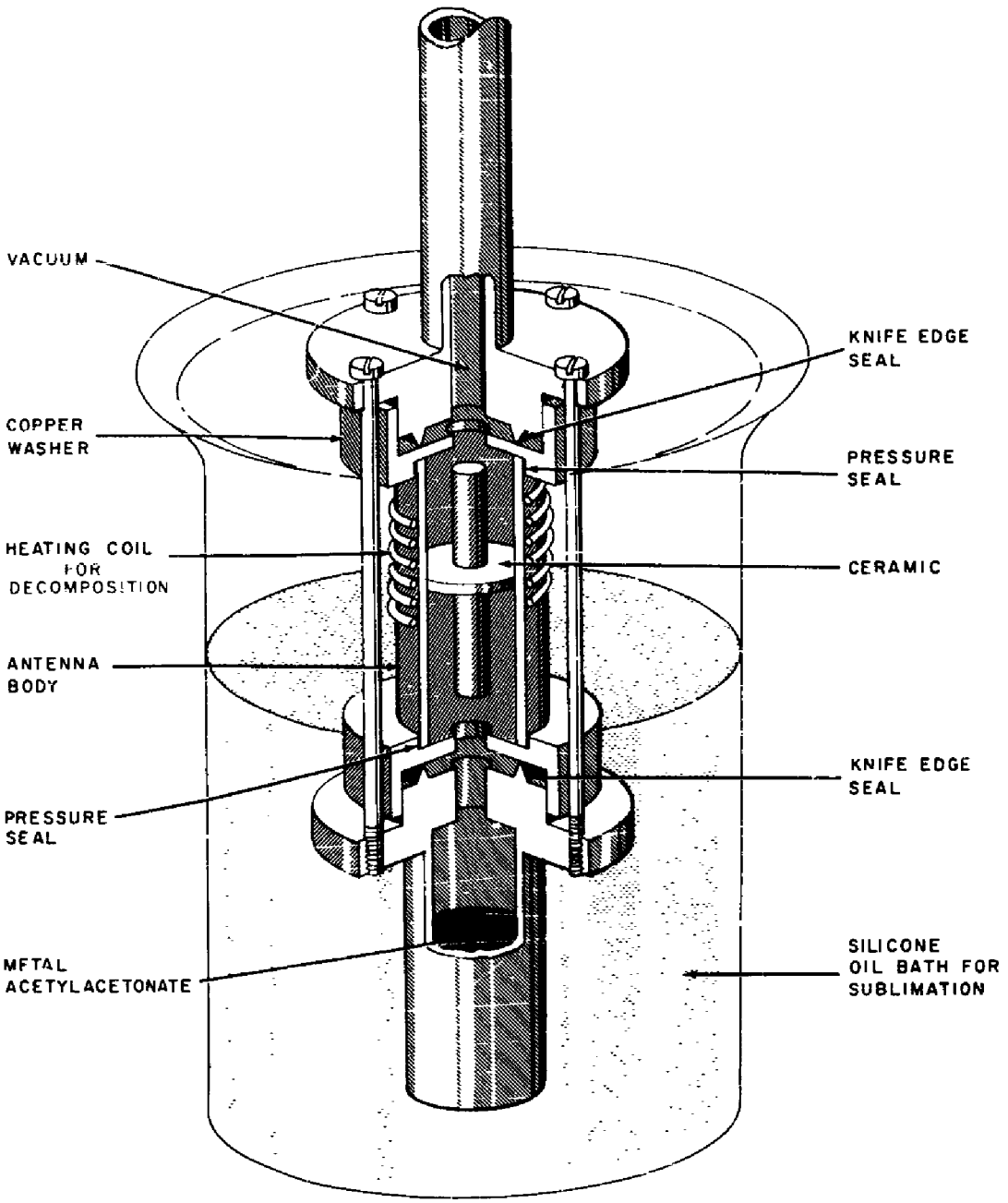


FIGURE 11. SUBLIMATION APPARATUS

(2) Animal and Vegetable Micro-Organisms. No specific investigation into these substances has been undertaken because of the problems which appear to be involved in their use. First, a proper penetrating vehicle for the substance would have to be chosen. Second, the difficulties involved in the use of penetrants, as mentioned in the previous section, would remain. In addition observation might be impossible at low power magnification It might also be mentioned that these substances would appear to require specialized handling which might be time consuming. If, however, other methods prove unsuccessful this approach will be explored further.

(3) Molten Indium and Mercury. These materials would prove useful either as recrystallized solids or solid solutions dispersed in the leak. However, one insurmountable problem is the surface tension of these materials (five to seven times that of water). It was mentioned previously that sucrose water solutions required pressure differentials in order to penetrate the leaks. Even with the use of ultrasonic vibration it is felt that these materials would not penetrate. No tests have been run with these materials but some work in this area may be required in the future.

(4) Pyrolysis of Gaseous Materials to Leave a Carbonaceous Residue. This approach will be the next area investigated if presently developed methods prove unsuccessful for smaller leaks. This approach was not previously attempted since it requires going to elevated temperatures before residue formation is completed.

(5) Radiographic Detection of High-Density Materials. A concentrated solution of lead acetate was forced into a large leak. More concentrated lead solutions may be obtained by adding leak nitrate to the acetate solution. An X-ray picture of this sample showed no detectable leak path, although the center pin could be moved freely. This method might still have proved successful if enlargements of the X-rays could be obtained. It is, however, limited in this area due to a loss of definition.

(6) Autoradiographic Technique. This technique involves the introduction of a radioactive material into the leak path in question. Assuming that the material would remain during sectioning, a photographic emulsion is placed in contact with the sectioned sample and the emulsion is sensitized in the area of radioactive material. The drawback of this technique is that no visible means of locating the leak path is available prior to sectioning. In addition, no magnification of the defect other than enlargement of the negative is available.

(7) Ultrasonic. Flaw detection is possible by passing high-frequency sound waves through a solid object and observing the reflection by use of an oscilloscope. A sound wave will pass through a solid homogeneous material and will be reflected when confronted with a material of different density. This may be a void or inclusion. This method is only applicable when homogeneous materials are involved. This rules out the possibility of testing most assemblies which are constructed of various metals and non-homogeneous ceramics.

Work is being continued in those areas which have shown the most promising results. Refinements are to be made in the introduction of carbonaceous materials and in the retention of these residues in the leak paths during metallographic preparation. The majority of the work however will be confined to the method involving the decomposition of metals from a gas. It is felt that this area of endeavor will yield the most rewarding results.

SECTION III

CONCLUSIONS

It has been illustrated that a statistical approach, based on an analysis of variance of basic factorial design, can be applied to a systematic study of the parameters effecting the reliability of ceramic-to-metal seals. Experiment No. 1 has shown that two types of nickel plating used on two types of ceramic, at two different thicknesses, will yield no significant difference in seal strength. It was concluded, therefore, that economy considerations should govern the type and thickness of plating used on metallized ceramics.

Axial alignment of the ceramic test specimen has been shown to be of major importance in obtaining reproducible tensile test data on ceramic-to-metal seal strength. Two methods have been found useful in the detection of leak paths in ceramic-metal assemblies. The first is the deposition of carbonaceous material by the decomposition of a hydrocarbon impregnated in the leak. The second is the deposition of metal in the leak path from a gaseous phase. It is concluded that both methods can be applied to a metallographic examination technique which will allow a categorizing of leak paths.

SECTION IV

PROGRAM FOR NEXT INTERVAL

During the third contract period the following activities are planned:

- The initial variable study, consisting of five experiments, will be completed.
- A refined variable study will be designed and started.
- The non-pumping, cold cathode, ion gage will be fabricated and tested. If found successful, materials will be ordered for test specimens.
- A leak path detection method will be optimized, and a statistically significant number of leaks examined to categorize leak mechanisms.
- The ceramic-to-metal sealing manual will be started.

DISTRIBUTION LIST

Project Engineer RADC Griffiss AFB New York	1
RAAP RADC Griffiss AFB, New York	1
RAALD RADC Griffiss AFB, New York	1
ROZMSTT RADC Griffiss AFB, New York	1
RAIS, Mr. Malloy For: Flt. Lt. Tanner RADC Griffiss AFB, New York	1
Signal Corps Liaison Officer RADC (RAOL, Capt Norton) Griffiss AFB, New York	1
AU (AUL) Maxwell AFB, Alabama	1
ASD (ASAPRD) Wright-Patterson AFB, Ohio	1
Chief, Naval Research Lab ATTN: Code 2021 Washington 25, D.C.	1
Air Force Field Representative Naval Research Lab ATTN: Code 1010 Washington 25, D.C.	1
Commanding Officer USASRDL ATTN: SIGRA/SL-ADT Ft. Monmouth, New Jersey	1
Chief, Bureau of Ships ATTN: Code 312 Main Navy Building Washington 25, D.C.	1
Office of the Chief Signal Officer Depart of the Army ATTN: SIGRD Washington 25, D.C.	1
AFPR Lockland Br. GE Co. PO Box 91 Cincinnati 15, Ohio	1
Chief, AF Section MAAG Germany Box 810 APO 80 New York, New York	1

DISTRIBUTION LIST (Continued)

AFSC (SCSE) 1
Andrews AFB
Washington 25, D. C.

ASTIA (TIPCA) 10
Arlington Hall Station
Arlington 12, Virginia

European GEEIA Region 1
(ZEM)
APO 332
New York, New York

Pacific GEEIA Region 1
(ZPM)
APO 323
San Francisco, California

Western GEEIA Region 1
(ZSM)
McClellan AFB,
California

Eastern GEEIA Region 1
(ZMM)
Brookley AFB,
Alabama

Central GEEIA Region 1
(ZOME)
Tinker AFB,
Oklahoma

GEEIA Region (ZSOEP) 1
2868th GEEIA Squadron
APO 942
Seattle, Washington

Eitel-McCullough 1
ATTN: Mr. George Caryotakis
301 Industrial Way
San Carlos, California

Globe-Union, Inc. 1
ATTN: Mrs. C. Wuthrich,
technical librarian assistant
900 East Keefe Avenue
Milwaukee 1, Wisconsin

Device Seals, Inc. 1
ATTN: Mr. Robert R. Terry
7225 Radford Ave.
North Hollywood, California

National Bureau of Standards 1
Section 14-2
ATTN: Mr. C. P. Marsden
Washington 25, D. C.

Carvil Technical Ceramics, Inc. 1
ATTN: Mr. V. G. Matto,
President
801 23rd Street
Union City, New Jersey

L. S. Nergaard 1
RCA Laboratories
Princeton, New Jersey

Watkins-Johnson Co. 1
ATTN: Mr. W. L. Talbot
3333 Hillview Ave.
Palo Alto, California

Corning Glass Works 1
ATTN: Mr. E. Lusk,
Product Engineer
Corning, New York